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THE EFFECT OF PROCEDURAL VARIABLES ON TG, DTG AND DTA CURVES OF MAGNESITE AND DOLOMITE

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TG, DTG and DTA curves of magnesite are dependent on procedural variables, especially sample mass, heating rate and partial pressure of carbon dioxide, in a similar manner to those of calcite [1], although the magnitude of the effect is less for magnesite. The first stage of the decomposition of dolomite varies with increasing partial pressure of carbon dioxide in an anomalous manner and hence the effects of these procedural variables (except heating rate) are not similar to those observed for magnesite and calcite. The second stage of the decomposition of dolomite is, however, strongly dependent on these procedural variables and behaves in a manner that would be predicted for a sample of calcite diluted with magnesia. A 1:1 molar mixture of magnesite and calcite also behaves as would be predicted from the behaviour of the single carbonates but differently from that of dolomite.

This study of the influence of procedural variables on TG, DTG and DTA curves of magnesite and dolomite follows on from that recently published concerning similar curves of calcite [1]. These three carbonates are closely related chemically and all have the same crystal structure. It has been shown, however, that the thermal decomposition of dolomite [2], and references therein is not the same as that predicted for a mixture of magnesite and calcite. Although it decomposes in two stages as follows:

$$CaMg(CO_3)_2 = CaCO_3 + MgO + CO_2 \qquad \text{(Stage 1)}$$

$$CaCO_3 = CaO + CO_2 \qquad \text{(Stage 2)}$$

the first stage takes place at a substantially higher temperature than that of magnesite and shows an anomalous dependence on the partial pressure of carbon dioxide in the atmosphere around the sample. The second stage, by contrast, follows closely the behaviour expected for the decomposition of calcite.

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The results reported here relate to the dependence of the thermal analysis curves on the mass of the sample, the partial pressure of carbon dioxide in the atmosphere and the influence of water vapour for both carbonates, and also that of heating rate for dolomite and that of an inert diluent for magnesite.

Experimental

The sample of magnesite selected for this study was a natural mineral, which showed no X-ray diffraction peaks other than those attributed to it in the literature and was of purity greater than 99%. The dolomite was also of high purity although it did contain a trace amount of free calcite. Both minerals were ground to less than 300 mesh British Standard sieve ($<55\,\mu$m).

The same TG and DTA equipment was used as in the recent paper on calcite [1] and similar experimental conditions were employed. The results of this investigation are, therefore, directly comparable with those previously reported for the decomposition of A.R. calcium carbonate and limestone.

Results

Effect of sample mass in an atmosphere of nitrogen

The effect of increasing the mass of the sample on the DTG and DTA peak temperatures of magnesite is shown in Table 1. The temperatures, $T_{0.1}$, $T_{0.5}$ and $T_{0.9}$, correspond to the temperatures at which the fraction reacted, x, reached 0.1, 0.5 and 0.9, respectively, (obtained from the TG curves of magnesite) are also listed in Table 1. The parameter x_m is the value of x at the DTG peak temperature.

It can be seen that variations in sample mass displaced the DTG and DTA curves of magnesite to higher temperatures and that the effect was similar in magnitude for both techniques. It was, however, a smaller effect than that observed when samples of A.R. calcium carbonate and limestone were heated under identical experimental conditions [1]. The increase was 30° for samples of magnesite (50 mg to 300 mg) studied by DTG and 25° by DTA, compared with an increase of the order of 90° for calcite.

Table 1 The effect of sample mass on the TG, DTG and DTA curves of magnesite in nitrogen atmosphere

Sample mass, mg	$T_{0.1}$	$T_{0.5}$	$T_{0.9}$	ΔT	x_m	DTG	DTA
						peak temperatures, °C	
50	565	608	635	70	0.61	615	638
100	–	–	–	–	–	–	642
200	–	–	–	–	–	–	655
300	595	645	678	83	0.50	645	663
200*	590	643	687	97	0.52	645	667

*pellet

The effect of similar variations in the mass of the sample on the first and second stages of the decomposition of dolomite is shown in Table 2. The increase in peak temperature (85° by DTG on increasing the sample mass from 50 mg to 300 mg) for the *second* peak was similar to that for calcite, but this was not the case for the first peak. Although the DTG peak temperature showed a large increase as the sample mass was increased from 50 to 100 mg further increases in mass caused little change in the DTG peak temperatures. This effect is shown even more graphically when the DTA peak temperatures are compared. These vary in an apparently random way with increase in the sample mass and are all within the narrow range from 790 to 802°. This temperature range is much higher than that shown in Table 1 for the decomposition of magnesite (638 to 667°). The carbon dioxide released during the first stage of the decomposition of dolomite at ca. 800° has affected the second DTA peak for the 50 mg sample, hence the smaller difference in second peak temperatures for dolomite from DTA (53°) than from DTG (85°); the DTG result is believed to be the more meaningful.

Some data for a 1:1 molar mixture of magnesite and calcite are shown in Table 3 for comparison with those for dolomite, which has the same chemical analysis. The mixture of the two single carbonates behaves in the manner predicted from the data obtained for magnesite and calcite, when heated alone. Thus the first stage was observed at 627° by both DTG and DTA, closely similar to the temperature predicted for an equivalent amount of magnesite (137 mg for DTG and 46 mg for DTA) from the data listed in Table 1. Similarly the values shown in Table 3 for the second stage of the decomposition of dolomite are close to those previously reported for equivalent amounts of calcite [1].

Table 2 The effect of sample mass on the DTG and DTA peak temperatures of the dolomite in a nitrogen atmosphere

Sample mass,	DTG peaks, °C		DTA peaks, °C	
mg	1st	2nd	1st	2nd
50	740	790	798	867
100	–	–	802	882
200	785	855	800	905
300	807	875	790	920
400	805	890	–	–
500	795	–	–	–
200*	807	875	800	910

*pellet

DTG curves obtained at a heating rate of 7 deg/min and DTA curves at 10 deg/min

Table 3 Peak temperatures for a 1:1 molar mixture of calcite and magnesite

Atmosphere	DTG paks, °C		DTA paks, °C	
	1st	2nd	1st	2nd
N_2 (1 atmos.)	627	863	627	848
CO_2 (0.1 atmos.) N_2 (0.9 atmos.)	630	890	–	–

DTG data based on 300 mg heated at 7 deg/min and DTA data based on 100 mg heated at 10 deg/min

DTG and DTA peak temperatures of 200 mg pelletized samples of magnesite and dolomite were almost identical to those of 300 mg powdered samples (Tables 1 and 2). This phenomenon was also observed for calcite and is related to the 'bed-depth' effect [1].

Effect of an inert diluent in a nitrogen atmosphere

This effect was studied by adding South African quartz (SiO_2) to the magnesite; previous studies [3] had shown that there was no appreciable reaction between silica and the magnesite used in this study prior to decomposition in both nitrogen and carbon dioxide atmospheres. From the results shown in Table 4 it can be seen that the effect of the diluent is negligible as the DTA peak temperature observed in the presence of the quartz was similar to that for an equivalent mass of magnesite heated alone, rather than that for a mass equal to the total mass of the sample. Further experiments were not carried out as this aspect has been thoroughly investigated by Warne and Mackenzie [4], whose conclusions are discussed below.

Table 4 The effect of dilution on the DTG peak temperatures of magnesite in a nitrogen atmosphere

Mass of $MgCO_3$, mg	Mass of SiO_2, mg	DTG peak, °C
50	–	615
50	250	612
300	–	645

Effect of carbon dioxide atmospheres

Results obtained for the decomposition of magnesite and dolomite in various atmospheres containing carbon dioxide are shown in Table 5. An increase in the partial pressure of carbon dioxide over the sample brought about an increase in the peak temperatures for magnesite, which once again was similar in magnitude for both DTG and DTA. The increase on replacing nitrogen by carbon dioxide was of the order of 20°, which was substantially less than that of about 70° reported for calcite [1].

In dramatic contrast to these results for calcite and magnesite, the temperature of the *first stage* of the decomposition of dolomite decreased when carbon dioxide was introduced into the atmosphere. DTG and DTA peak temperatures for a wide range of partial pressures of carbon dioxide, studied at various heating rates, have been reported previously (Table 1 of Ref. 2). The minimum temperature varied with the sample mass and heating rate used, but it can be seen from the data shown in Table 5 that the peak was observed to be about 30° lower in 0.1–0.2 atmos. of carbon dioxide than in nitrogen, and indeed was still significantly lower in 1 atmos. of carbon dioxide than it was in 1 atmos. of nitrogen. On the other hand, the *second stage* of the decomposition of dolomite followed the expected dependence on partial pressure of carbon dioxide. The results shown in Table 5 are very similar to those predicted for equivalent amounts of calcite, i.e. 163 mg of calcite from a 300 mg sample of dolomite (as used in the DTG runs) and 54 mg from a 100 mg sample (DTA). It can be concluded that the first stage of the decomposition of dolomite has an anomalous dependence on the partial pressure of carbon dioxide, as has been more fully discussed elsewhere [2, 5], but the second stage behaves as would be predicted for a sample of calcite diluted with magnesia formed during the first stage of the decomposition.

Table 5 The effect of the partial pressure of carbon dioxide on the peak temperatures for magnesite and dolomite

Atmosphere		Magnesite		Dolomite			
CO_2	N_2	DTG	DTA	1st peak		2nd peak	
		peak temperatures, °C		DTG	DTA	DTG	DTA
–	1.0	645	642	807	802	875	882
0.1	0.9	660	648	770	780	887	885
0.2	0.8	660	650	777	768	910	892
1.0	–	665	660	790	773	955	943
ΔT		20	18	–17	–29	80	61

ΔT is the difference in temperature between T_m for the sample heated in 1 atmos. CO_2 and that heated in 1 atmos. N_2
DTG data obtained on 300 mg samples heated at 7 deg/min
DTA dataobtained on 100 mg samples heated at 10 deg/min

Effect of heating rate

This effect was not investigated for magnesite, but was investigated for dolomite and the results are shown in Table 6. It can be seen that this was an important variable and that the DTG peaks in an atmosphere of nitrogen and in those containing carbon dioxide were displaced to substantially higher temperatures when the heating rate was increased from 1 to 7 deg·min^{-1}. Both the first and second stages of the decomposition were affected by 60–70°, except for the second stage in 1 atmosphere of carbon dioxide which was displaced by only 30°.

Effect of water vapour in the atmosphere

Results already presented [2] indicate that the presence of water vapour in an atmosphere of either nitrogen or carbon dioxide lowers the peak temperature for magnesite as determined by both DTA and DTG. The lowering is of the order of 15°, which is closely similar to that reported for calcite in nitrogen, although the value for calcite heated in carbon dioxide was little changed [1, 2]. DTA curves for dolomite heated in a wet atmosphere of nitrogen had a higher peak temperature than in dry nitrogen for the first stage of the decomposition, but a lower peak temperature for the second stage [2]. Once again the first stage has been observed to behave in a manner different from that of magnesite, although the second stage behaved in a similar way to that of calcite. In contrast, in atmospheres containing carbon dioxide (0.1–1.0 atmos.) DTA peak temperatures increased in wet atmospheres compared with dry for both stages of the decomposition. The increase was about 20° for the first peak and about 5° for the second peak [2, Table 5].

Table 6 The effect of heating rate on the DTG peak temperatures of dolomite (300 mg)

Atmosphere	Heating rate, deg/min	DTG peak temperatures, °C	
		1st	2nd
N_2 (1 atmos.)	1	745	805
N_2 (1 atmos.)	7	807	875
CO_2 (1 atmos.)	1	730	925
CO_2 (1 atmos.)	7	790	955

Discussion

The results presented in the previous section clearly demonstrate in a quantitative manner that procedural variables influence TG, DTG and DTA curves of magnesite. Qualitatively the effects are similar to those observed for limestone and A.R. calcium carbonate [1], but they are much smaller in magnitude. For example, when the mass of the sample was increased from 50 mg to 300 mg in the case of calcite, the DTG and DTA peak temperatures in nitrogen increased by 80–95° [1], whereas in the case of magnesite the increase was only 25–30° (Table 1). The 'bed-depth' effect is, therefore,reduced for the decomposition of magnesite compared with that of calcite, which may be because the decomposition of magnesite is less readily reversible and hence not as greatly affected by the back-pressure of carbon dioxide. Once again the behaviour of a 200 mg sample in the form of a pellet was similar to that of a 300 mg sample in powdered form. This observation applies to the decomposition of calcite, magnesite and to both stages of that of dolomite.

The DTG and DTA curves of a 1:1 molar mixture of magnesite and calcite showed two peaks at approximately the temperatures expected for equivalent quantities of each component diluted with an inert material. The behaviour of the double carbonate of magnesium and calcium (viz. dolomite) is, however, entirely different. The first peak associated with the decomposition into magnesia and calcite is observed at a much higher temperature in the double carbonate than in the mixture of the two single carbonates. Furthermore, it is observed at a lower temperature in an atmosphere containing carbon dioxide than it is in an atmosphere of nitrogen. The unusual effects reported here for the first stage of the decomposition of dolomite (Tables 2 and 5) can be accounted for in terms of the anomalous thermal decomposition discussed by the present authors in a separate paper [2]. The second stage of the decomposition, on the other hand, behaves as would be predicted for calcite diluted with magnesia, and the temperature of the second peak increased with increasing sample mass in a similar way to that already reported for calcite [1]. The temperatures observed are almost exactly those that would be predicted for the quantity of calcite liberated during the decomposition of dolomite.

Some years ago Gokhale and Rao [6] claimed that the presence of magnesite in dolomite appreciably reduced the decomposition temperature of the first peak of the dolomite decomposition. Their evidence for this statement was that 'while the peak of the dissociation of pure synthetic dolomite was at about 798°, a significant shift to 732° was noticed in mixtures of magnesite with 10% dolomite'. In the course of the present investigation we have observed that the DTG peak of 500 mg of dolomite heated at 7 $\mathrm{deg \cdot min^{-1}}$ in nitrogen was at 795°, whereas a 50 mg sample under the same conditions was at 740°. These values are strikingly similar to those reported by Gokhale and Rao [6] and indicate that the shift in temperature that they observed was due merely to dilution of the sample of dolomite by incorporation of magnesite. This conclusion confirms that of Warne and Mackenzie [4].

The effect of water vapour in the atmosphere has been discussed elsewhere [2]. The behaviour of magnesite was similar to that of calcite, but that of dolomite was different. The presence of water vapour in the atmosphere affected the crystallite size of the reaction product. It seems probable that the observed differences are associated with different stages of surface sintering reached by the various samples.

Conclusions

1. TG, DTG and DTA curves for the decomposition of magnesite are dependent on procedural variables, particularly on sample mass, heating rate (although not studied here) and the partial pressure of carbon dioxide. The magnitude of these effects is similar for DTG and for DTA, in accordance with the bed-depth effect discussed previously [1].

2. The effects of sample mass and of partial pressure of carbon dioxide on the decomposition of magnesite are less than those observed in the case of the decomposition of calcite [1].

3. The first stage of the decomposition of dolomite varies with increasing partial pressure of carbon dioxide in an anomalous manner [2, 5] and hence

similar effects of these procedural variables to those reported for calcite and magnesite are not observed.

4. These procedural variables do, however, have the expected effect on the second stage of the decomposition of dolomite, which behaves as predicted for a sample of calcite diluted with magnesia.

5. An inert diluent has little effect on the decomposition temperature, since it causes no increase in the partial pressure of carbon dioxide within the powder bed. Magnesite and calcite behave in a similar way with respect to dilution.

6. The decomposition of magnesite was observed at lower temperatures in wet atmospheres, whereas that of dolomite was observed at higher temperatures (except for the first stage in nitrogen). These observations seem to be associated with different crystal growth and sintering behaviour.

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References

1 F. W. Wilburn, J. H. Sharp, D. M. Tinsley and R. M. McIntosh, J. Thermal Anal., 37 (1991) 2003.
2 R. M. McIntosh, J. H. Sharp and F. W. Wilburn, Thermochim. Acta, 165 (1990) 281.
3 F. W. Wilburn and C. V. Thomasson, Phys. Chem. Glasses, 2 (1961) 126.
4 S. St. J. Warne and R. C. Mackenzie, J. Thermal Anal., 3 (1971) 49.
5 W. R. Bandi and G. Krapf, Thermochim. Acta, 14 (1976) 221.
6 K. V. G. K. Gokhale and T. C. Rao, J. Thermal Anal., 2 (1970) 83.

Zusammenfassung — TG-, DTG- und DTA-Kurven von Magnesit sind ähnlich wie bei Kalzit [1] abhängig von den Versuchsparametern, besonders von Probenmasse, Aufheizgeschwindigkeit und Partialdruck von Kohlendioxid, obwohl das Ausmaß dieses Einflusses bei Magnesit geringer ist. Der erste Schritt der Zersetzung von Dolomit ändert sich in einer ungewöhnlichen Weise durch Erhöhung des Partialdruckes von Kohlendioxid und deshalb unterscheidet sich der Einfluß dieser Versuchsparameter (mit Ausnahme der Probenmasse) von dem, der bei Magnesit und Kalzit beobachtet wurde. Der zweite Schritt bei der Zersetzung von Dolomit ist stark von diesen Versuchsparametern abhängig und verläuft so, wie man es für eine mit Magnesia verdünnte Kalzitprobe voraussagen würde. Eine Gemisch aus Magnesit und Kalzit im Verhältnis 1:1 verhält sich ebenso, wie man es auf Grund des Verhaltens der einfachen Karbonate voraussagen würde, unterscheidet sich jedoch von dem des Dolomits.